



Molecular Orientation and the Partial Vapor Pressures of Binary Mixtures

EDWARD WILLIAM ENGEL

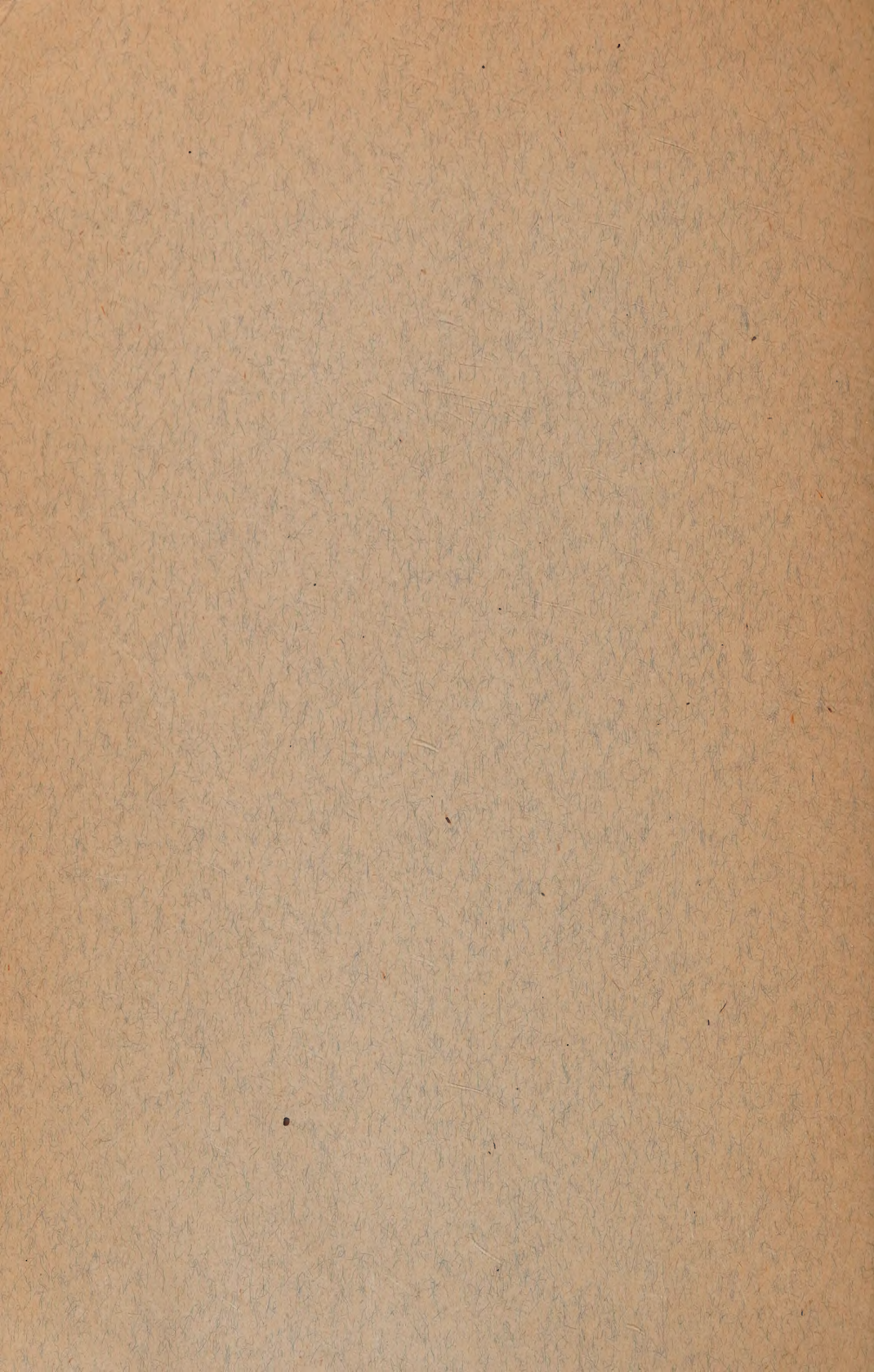
Princeton



3781
P95 E

UNCLASSED

Microfilm



Molecular Orientation and the Partial Vapor Pressures of Binary Mixtures

A DISSERTATION

PRESENTED TO THE

FACULTY OF PRINCETON UNIVERSITY
IN CANDIDACY FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

BY

EDWARD WILLIAM ENGEL

EASTON, PA.
MACK PRINTING COMPANY
1929

Accepted by the Department of Chemistry,
April 1, 1928.

MOLECULAR ORIENTATION AND THE PARTIAL VAPOR PRESSURES OF BINARY MIXTURES.

I. SYSTEMS COMPOSED OF NORMAL LIQUIDS

Although many measurements have been made of the vapor pressures of solutions containing but one volatile component and the total vapor pressures of great numbers of binary mixtures of volatile liquids have been determined, few experimental data are available on the partial pressures of binary liquid mixtures. Many partial pressures have been calculated from total pressures by means of equations, theoretical and empirical, the success of the calculations depending not only upon the nature of the equations but, unfortunately, upon that of the mixtures as well. An equation recently developed by Langmuir¹ seemed to offer a means not merely of calculating partial pressures but also of learning much about the molecular condition of liquids. In order to examine the applicability of this equation and in order to gain information which might be coordinated with the results of studies of the dielectric polarization of liquids, the measurement of partial vapor pressures was undertaken.

Apparatus and Procedure

The apparatus employed (Fig. 1) was similar in many respects to that used by Sameshima.² The vessel A, which had a capacity of 200 cc., contained the liquid mixture, the partial vapor pressures of which were to be measured. A was immersed to the level of the ground-glass stopper S in a carefully regulated thermostat, the temperature of which was approximately 2° above the temperature at which the pressures were to be measured. Superheating was prevented by stirring the liquid electrically by means of a current through platinum spiral B, which was carried by a tube entering the vessel through a ground joint with a mercury seal. The temperature of the boiling liquid was read on the thermometer T, which was suspended by a platinum wire from a hook on the stopper S. The thermometers used were of short range, calibrated in fifths of a degree and standardized at the U. S. Bureau of Standards. The large side tube C was wound with an electric heater, which prevented the condensation of any vapor in C and its subsequent direct return to A. The condensers, D and D', were surrounded by insulated copper jackets, E and E', which were filled with solid carbon dioxide in the form of "dry ice." The low temperature obtained with the solid carbon dioxide prevented the escape of vapor and consequent change in the composition of the liquid, which occurred in the preliminary experiments when ice was used for the condensation of the more volatile liquids. In the case of liquids of high freezing point, solidification in the condenser was prevented by inserting a thin sheet of asbestos between the condenser bulbs and the "dry ice." The vapor condensed in D flowed down into the bulb

¹ Langmuir, "Third Colloid Symposium Monograph," The Chemical Catalog Company, Inc., New York, 1925, p. 3.

² Sameshima, *J. Am. Chem. Soc.*, **40**, 1482 (1918).

F, which had a capacity of about 4 cc. The bulb ordinarily filled within three minutes after the liquid had begun to boil in A and then overflowed through G back into A.

With the aid of the carboys, H and J, which functioned as stabilizers, the pressure was maintained constant during a run by means of the manometer K and a rotary oil pump. When the pressure had been lowered by the pump to a point where the liquid in A boiled at the desired temperature, the platinum wire L, sealed through a small glass tube and attached to a length of copper wire, was adjusted so that its end was at the top of the mercury column, the adjustment being made by sliding the copper wire through the soft wax seal X. This wire and the wire sealed into the manometer at K were connected through a relay, which turned the pump off and on as the mercury column made or broke contact with the wire L, at its surface, the pressure thus being kept so constant that no variations could be observed on the manometer N.

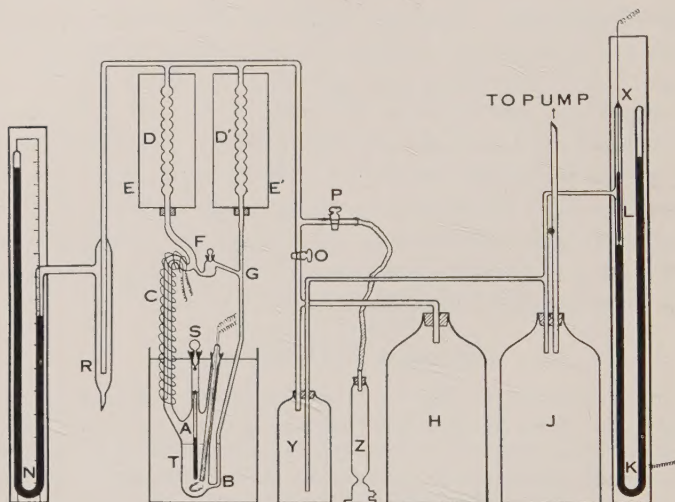


Fig. 1.—Apparatus for vapor pressure measurements.

In order to avoid pressure gradient between A and the manometer N, the tubing used was, for the most part, of 10-mm. internal diameter. The trap R was inserted to keep any liquid which might get into the upper part of the apparatus from running down into the manometer, but this precaution proved unnecessary. The stopcocks O and P were employed to open the main apparatus to atmospheric pressure, while maintaining low pressure in the carboys when desired. Bottles Y and Z contained calcium chloride.

A measurement was carried out in the following manner. About 100 cc. of a mixture, the composition of which was approximately that desired, was placed in Vessel A. The pressure was gradually reduced until, when the electrical stirrer was turned on, the liquid began to boil. The pressure was then regulated until the thermometer constantly indicated the desired temperature. The liquid was allowed to boil for some time, the temperature being kept under careful surveillance. It was found that five or ten minutes were normally sufficient for the attainment of equilibrium conditions, but, for the sake of safety, thirty or forty minutes were usually allowed. The liquid condensed in F now had the composition of the vapor in equilibrium with the liquid in A; 3- or 4-cc. samples were pipetted out of A and F and analyzed by the measurement of their

refractive indices as was done by Zawidski.³ If the mole fractions of the two components of the liquid in F were A and B and the total pressures read on Manometer N were P, the partial pressures of the liquid in Vessel A were AP and BP.

Because of deviations from the ideal gas laws, the partial pressures calculated in this manner are not identical with the pressures which the vapors of the components would exert if allowed to occupy the same volume separately.⁴ The results of other investigators have shown that these deviations cause errors of less than 1% in the apparent molecular weights of a large number of vapors measured between 70 and 100°, and Sameshima² has found the deviations in mixtures of ether and acetone vapors at 25° to be so small as to be without appreciable effect upon the values of the partial pressures calculated upon the assumption of the applicability of Dalton's law. Even though the deviations may have an appreciable effect in some of the mixtures here studied, the effect should be too slight to impair the use of the results in the examination of Langmuir's theory.

The indices of refraction for the sodium D line were measured with a Pulfrich refractometer, a temperature of 20°, constant within 0.01°, being obtained by a flow of water from carefully adjusted thermostats. The probable error of a measurement was 0.00007. For a given system from twelve to fifteen mixtures of known composition were made up and measured. The molar composition of the mixture corresponding to the observed refractive index if the refractive index were a linear function of composition was calculated and subtracted from the known composition. The differences between the theoretical and the known mole fractions obtained in this way were plotted against the theoretical mole fractions to give a curve which was used to correct the theoretical composition of an unknown mixture of the two liquids calculated from the refractive index on the assumption that the latter was a linear function of the composition. The accuracy of this method of analysis depended upon the precision of the index measurements and upon the difference between the indices of the two components of the mixture. The probable error in the mole fraction was usually 0.001–0.003. The probable error of the partial pressure data was somewhat dependent upon the nature of the liquids under investigation and upon the temperature of the measurement, but was normally 2 ± 1 mm.

In order to ascertain whether or not the apparatus functioned properly, the system benzene–carbon tetrachloride was investigated, the partial pressures being found to duplicate the measurements of Zawidski within the experimental error.³ The vapor pressure–temperature curves obtained for a number of the pure substances under investigation were found to agree well with the data in the literature.

Purification of Materials

The purification of the materials used is described below. Under each material are given the values of physical constants which serve as criteria of purity. In addition to the boiling point and the refractive index for the sodium D line at 20°, the melting point and the density were occasionally measured. The vapor pressures measured at several temperatures agree well with those given in Landolt-Börnstein, "Tabellen," 5th ed., Berlin, 1923, as previously remarked.

n-Hexane.—A synthetic product obtained from the Eastman Kodak Company was washed repeatedly with slightly diluted sulfuric acid, then with alkaline permanganate solution, dried over sodium, and distilled; b. p. 68.8°; $d_4^{20} = 0.6600$; $n_D^{20} = 1.37508$.

³ Zawidski, *Z. physik. Chem.*, **35**, 129 (1900).

⁴ Dolezalek and Schulze, *Verhandl. deut. physik. Ges.*, **14**, 1091 (1912); Schulze, *ibid.*, **15**, 488 (1913); *Physik. Z.*, **14**, 922 (1913).

***n*-Heptane.**—Material obtained from the Ethyl Gasoline Corporation was found to require no purification; m. p. -90.5° ; b. p. 98.4° ; $d_4^{20} = 0.6838$; $n_D^{20} = 1.38767$.

Carbon Tetrachloride.—The best product obtainable from Merck was dried over fused calcium chloride and distilled. A fraction boiling constantly at 76.4° was employed; b. p. 76.4° ; $n_D^{20} = 1.46026$.

***n*-Butyl Chloride.**—A material of good quality obtained from the Eastman Kodak Company was refluxed gently for half an hour over an equal volume of concentrated sulfuric acid, distilled, washed with water until free of sulfate, dried over fused calcium chloride and fractionated. A fraction boiling from 77.3 to 77.6° was employed; $n_D^{20} = 1.40173$.

Ethyl Bromide.—A material obtained from the Eastman Kodak Company was washed several times with cold, concentrated sulfuric acid, then with water until all sulfate was removed, dried over fused calcium chloride and fractionated. The fraction boiling at 38.3 – 38.4° was employed. Two lots thus prepared gave values of 1.42403 and 1.42408 for the refractive index; $d_4^{20} = 1.4586$; $n_D^{20} = 1.42405$.

Ethyl Iodide.—A material obtained from Merck was washed with a very dilute caustic potash solution until decolorized. Several drops of the caustic solution were added in excess and the material was then separated, thoroughly washed with water, dried over fused calcium chloride and fractionated. A fraction distilling without any perceptible change in temperature at 73.2° was employed. The vapor pressure of this material, 355.0 mm. at 50° , differs from Regnault's value 364.0 mm. given in Landolt-Börnstein, "Tabellen," but agrees satisfactorily with the more accurate value of Zawidski, 353.4 mm.; b. p. 73.2° ; $d_4^{20} = 1.9292$; $n_D^{20} = 1.51330$.

***n*-Butyl Bromide.**—Material obtained from the Eastman Kodak Company was washed with cold concentrated sulfuric acid, then with sodium carbonate solution, dried over fused calcium chloride and fractionated. A fraction boiling from 100.4° to 100.6° was employed; $n_D^{20} = 1.43984$.

Ethyl Alcohol.—Ordinary 95% alcohol was refluxed over quicklime to which a small stick of sodium hydroxide was added. The refluxing was continued for 75–100

TABLE I
VAPOR PRESSURES OF PURE LIQUIDS (MM. OF HG)

<i>t</i> , °C.	Hexane	Ethyl iodide	Butyl chloride	Butyl bromide
20.0	...	...	31.3	82.3
30.0	186.1	162.6	51.0	130.2
40.0	275.7	244.8	52.2	198.5
50.0	400.6	355.0	126.7	295.8
60.0	568.0	505.9	189.6	420.7
70.0	...	...	271.3	591.4

<i>t</i> , °C.	Heptane	<i>t</i> , °C.	Carbon tetrachloride	<i>t</i> , °C.	Ethyl alcohol
22.7	41.4	19.2	88.0	22.7	51.8
30.0	58.2	32.4	156.0	32.6	90.1
30.3	58.8	41.2	222.8	35.7	105.6
38.4	86.0	50.0	312.0	41.8	145.1
50.0	141.1	60.8	452.8	57.2	306.8
51.2	150.0	68.7	586.4	59.6	342.7
61.2	220.0	76.4	760.0	69.4	531.1
69.5	297.8	..	...	78.1	747.6
70.0	301.4	..	...	78.4	760.0
79.5	419.7	..	...	..	...
98.4	760	..	...	..	...

TABLE II

PARTIAL VAPOR PRESSURES OF BINARY MIXTURES (MM. OF Hg)								
(A) 50° (B) Hexane-Heptane			(A) 50° (B) Heptane-Ethyl iodide			(A) 30° (B) Heptane-Ethyl iodide		
B	p _A	p _B	B	p _A	p _B	B	p _A	p _B
0	400.6	0	0	141.1	0	0	58.2	0
0.1136	359.3	14.2	0.0672	131.6	35.7	0.0927	54.6	27.3
.2787	282.1	43.2	.1095	124.8	64.2	.1628	50.9	42.6
.3583	252.0	51.9	.1692	116.4	92.4	.2458	47.5	58.1
.4328	222.9	58.7	.2253	108.1	119.9	.2965	44.4	69.6
.5163	187.7	73.9	.3116	99.5	154.1	.3548	42.1	79.3
.6702	120.4	99.3	.3793	90.8	180.1	.4134	39.5	87.9
.8586	53.9	123.1	.4277	85.1	196.2	.4836	37.0	95.9
1.0000	0	141.1	.4993	80.2	215.3	.5281	33.4	103.5
			.5119	76.4	222.4	.5738	31.9	109.0
			.5791	72.6	236.5	.6124	31.6	112.1
(A) 50° (B) Heptane-Butyl chloride			.6641	60.8	260.1	.7056	24.2	125.6
0	140.0	0	.7696	47.8	285.8	.7743	20.9	133.7
0.0496	135.2	17.2	.8272	39.9	301.2	.8325	17.4	140.6
.1128	129.4	37.8	.8783	37.6	309.4	.8892	12.8	147.1
.1580	118.9	63.9	.9426	16.3	336.3	1.0000	0	161.8
.2870	105.5	96.2	.9805	6.3	347.7			
.3853	93.9	123.7	1.0000	0	354.1			
.4462	85.6	143.4						
.5273	72.4	167.2				(A) 30° (B) Ethyl bromide-Ethyl iodide		
.5955	63.8	184.4				0	560.9	0
.6386	57.6	197.6				0.0406	538.2	3.8
.6979	50.4	212.1				.0895	509.6	13.9
.7797	39.5	231.7				.1445	479.8	24.4
.8645	25.2	255.0				.2096	442.0	36.7
.9565	11.5	277.3				.2579	411.7	46.4
1.0000	0	294.2				.3131	384.0	56.0
			(A) 50° (B) Butyl chloride-Butyl bromide			.3557	358.7	64.3
(A) 50° (B) Carbon Tetrachloride-Heptane			0	295.8	0	.3941	334.2	72.4
0	308.5	0	0.0501	276.5	5.4	.4327	312.5	79.8
0.0351	301.5	2.6	.1380	250.9	16.8	.4683	292.7	87.0
.1008	279.7	15.7	.2498	217.2	32.5	.4948	274.2	92.5
.1874	254.2	28.2	.3280	194.3	41.8	.5523	242.3	103.6
.2677	231.9	39.2	.4222	167.2	53.4	.5786	226.9	108.9
.3504	206.9	50.0	.4878	151.3	58.2	.6103	207.6	114.6
.4300	183.9	60.8	.5009	145.7	61.4	.6419	190.5	119.7
.4988	162.6	69.7	.5481	126.9	72.8	.6615	180.9	123.0
.5676	142.4	78.3	.6334	100.5	83.5	.7027	159.1	129.2
.6431	120.4	87.0	.7082	83.4	90.1	.7402	136.9	133.8
.6976	104.9	93.8	.7554	70.6	95.8	.8253	97.0	136.5
.8286	59.8	114.2	.8226	50.0	103.5	.8693	73.7	148.3
.9017	34.5	125.3	.8924	27.9	113.6	.9161	35.1	155.5
.9668	11.7	135.0	.9583	10.7	120.9	1.0000	0	161.8
1.0000	0	140.5	1.0000	0	126.7			

TABLE II (Concluded)

(A) 50° (B) Heptane-Butyl bromide			(A) 30° (B) Heptane-Ethyl bromide			(A) 30° (B) Hexane-Heptane		
<i>B</i>	<i>p_A</i>	<i>p_B</i>	<i>B</i>	<i>p_A</i>	<i>p_B</i>	<i>B</i>	<i>p_B</i>	<i>p_B</i>
0	140.0	0	0	58.0	0	0	186.1	0
0.1171	125.8	19.6	0.0923	55.7	66.3	0.1136	163.9	7.1
.2362	110.6	37.8	.2176	48.6	151.1	.2012	147.4	11.4
.3329	98.4	51.1	.2843	44.1	195.7	.3583	118.5	21.4
.4323	86.1	62.8	.3246	43.4	217.6	.4328	103.7	26.1
.5182	74.8	72.6	.4621	34.9	302.2	.5314	84.8	31.5
.5836	66.4	80.0	.4723	34.0	306.3	.6320	65.2	38.9
.6333	59.6	85.9	.6219	26.7	377.3	.6953	52.7	42.3
.6588	57.3	87.5	.7985	17.4	456.8	.8339	27.6	50.1
.7123	49.0	94.5	.9540	7.5	536.4	1.0000	0	58.0
.7935	37.2	102.6	1.0000	0	567.8			
.8805	23.3	112.2						
.9521	9.6	121.2						
0	0	127.0						

hours, the lime being renewed four or five times. An exceptionally good quality of powdered lime was finally used and the material distilled off; b. p. 78.4–78.5°; $n_D^{20} = 1.36130$.

n-Butyl Alcohol.—Material obtained from the Commercial Solvent Corporation was refluxed over lime and twice fractionated. A fraction boiling between 117.1 and 117.2° was employed; $n_D^{20} = 1.39942$.

Results

The vapor pressures of several pure liquids are given in Table I and in Table II are the partial vapor pressures of the binary mixtures. In a system A–B the less polar liquid is, as a rule, designated as A, but where there is no polarity or little difference in polarity, other considerations may determine the order. For each system the column under B gives the mole fraction of component B in the mixture and the columns under p_A and p_B give the partial pressures of components A and B over the mixture.

Langmuir¹ has employed the principle of independent surface action to derive the following expressions for the partial vapor pressures of a mixture of two liquids, A and B

$$p_A = P_A A e^{S_A \varphi \beta^2 / kT} \text{ and } p_B = P_B B e^{S_B \varphi \alpha^2 / kT} \quad (1)$$

in which p_A and p_B are partial pressures of Components A and B, respectively; P_A and P_B are vapor pressures of the pure liquids A and B, respectively; A and B are mole fractions of components A and B; S_A and S_B are surface areas of molecules of A and B; α and β are surface fractions of Components A and B

$$\alpha = \frac{S_A A}{S_A A + S_B B} \text{ and } \beta = \frac{S_B B}{S_A A + S_B B} \quad (2)$$

k is the Boltzmann constant $= 1.372 \times 10^{-16}$; T is the absolute temperature; and φ the "mixture energy," is a constant, dependent upon the molecular surface energies and independent of concentration.

For a mixture of two liquids, A and B, the molecules of one of which substances are enclosed by two kinds of surface, A and C, those of the other being enclosed by surfaces B and D

$$\varphi = ab\gamma_{ab} + ad\gamma_{ad} + bc\gamma_{bc} + cd\gamma_{cd} - ac\gamma_{ac} - bd\gamma_{bd} \quad (3)$$

in which a and c are the fractions of the surface of molecule A which are A-surface and C-surface, respectively, and b and d are the fractions of the surface of molecule B which are B-surface and D-surface, while γ_{ab} is the energy per sq. cm. of interface between surfaces A and B, γ_{ad} is the energy per sq. cm. of interface between A and D, etc.; φ is shown to be the energy per sq. cm. of molecular surface required for the transfer of a molecule of A from pure liquid A to pure liquid B or for the transfer of a molecule of B from pure liquid B to pure liquid A. The somewhat hypothetical surface areas of the molecules, expressed in square Ångströms (10^{-16} cm.²) are calculated from the densities by supposing that the liquids consist of close-packed spheres and the fractions of molecular surface, a , b , c , etc., used in the present paper are estimated from a comparison of the values of $V^{2/3}$ for the different groups, where V is the molar volume of the group at the boiling point of the liquid. It is assumed that the areas of the different kinds of surfaces in contact with one another are proportional to the fractions of the molecular surfaces involved, thus being calculable on the basis of a random orientation of the molecules. The value of γ for a certain kind of surface in a molecule is regarded as independent of the nature of the rest of the molecule. Thus γ should be the same for a hydrocarbon surface whether it be that of the heptane molecule or of the ethyl group in the ethyl alcohol molecule or of the butyl group in butyl chloride. Similarly, the energy per sq. cm. at a chlorine-hydrocarbon interface should be the same whether the chlorine is in carbon tetrachloride or butyl chloride, and whether the hydrocarbon is in another butyl chloride molecule or an alcohol or a heptane molecule. For binary mixtures in which fewer kinds of surface are involved, Equation 3 is simplified by the elimination of some of the terms, as will appear when it is applied to the results of the present investigation, in which only two or three kinds of surface are generally involved. This makes it possible to calculate the values of γ when φ is obtained for different mixtures.

Equation 1 may be written in the form

$$\varphi = 2.303 \frac{kT}{S_A \beta^2} \log \frac{p_A}{P_A A} \text{ and } \varphi = 2.303 \frac{kT}{S_B \alpha^2} \log \frac{p_B}{P_B B} \quad (4)$$

and used to calculate the value of φ , which, if the assumptions of the theory were rigidly correct, should be constant and the same for both partial pressure curves. Since the values of φ are greatly affected by experimental error, particularly at the ends of the partial pressure curves, it has seemed best to interpolate the values of p_A and p_B at intervals of 0.1 in the mole fraction and, for the sake of comparison, to designate the values of

φ calculated from the one partial pressure curve as φ_A and those from the other curve as φ_B . In Table III the first column gives the mole fractions of Component B from 0.1 to 0.9, and the succeeding columns give, for different systems, the values of p_A/p_{AA} and p_B/p_{BB} and the values of φ calculated from them. The deviations of p_A/p_{AA} and p_B/p_{BB} from 1 measure the deviations of the mixtures from Raoult's law.

TABLE III

VALUES OF p_A/p_{AA} , p_B/p_{BB} AND φ

<i>B</i>	(A) 50° (B) Carbon tetrachloride-heptane $P_A = 308.5$ $P_B = 140.5$				(A) 50° (B) 50° Heptane-butyl chloride $P_A = 140.0$ $P_B = 294.2$			
	p_A/p_{AA}	p_B/p_{BB}	φ_A	φ_B	p_A/p_{AA}	p_B/p_{BB}	φ_A	φ_B
0.1	1.008	1.068	1.89	0.25	1.032	1.156	1.15	0.57
.2	1.014	1.068	.86	.34	1.044	1.156	2.41	.71
.3	1.028	1.043	.81	.30	1.060	1.132	1.90	.77
.4	1.040	1.015	.68	.15	1.071	1.095	1.45	.75
.5	1.057	0.996	.65	— .01	1.092	1.074	1.17	.86
.6	1.077	.996	.64	— .02	1.124	1.053	1.05	.92
.7	1.107	.991	.68	— .08	1.178	1.055	1.05	1.05
.8	1.110	.992	.46	— .19	1.250	1.018	1.07	1.20
.9	1.151	.996	.64	— .32	1.358	1.012	1.05	2.94

<i>B</i>	(A) 30° (B) Heptane-ethyl bromide $P_A = 58.0$ $P_B = 567.8$				(A) 50° (B) Heptane-butyl bromide $P_A = 140.0$ $P_B = 127.0$			
	p_A/p_{AA}	p_B/p_{BB}	φ_A	φ_B	p_A/p_{AA}	p_B/p_{BB}	φ_A	φ_B
0.1	1.034	1.285	5.22	1.21	1.014	1.402	5.80	1.42
.2	1.078	1.221	4.64	1.08	1.028	1.299	2.79	1.34
.3	1.132	1.196	4.06	1.22	1.047	1.237	1.98	1.38
.4	1.149	1.180	3.48	1.42	1.072	1.165	1.58	1.29
.5	1.241	1.133	2.90	1.41	1.103	1.114	1.41	1.27
.6	1.293	1.080	2.32	1.24	1.143	1.075	1.28	1.27
.7	1.322	1.039	1.74	1.00	1.214	1.048	1.31	1.41
.8	1.379	1.009	1.16	0.49	1.300	1.016	1.29	1.03
.9	1.550	0.990	0.58	— 1.94	1.428	0.998	1.33	— 0.12

<i>B</i>	(A) 50° (B) Heptane-ethyl iodide $P_A = 141.1$ $P_B = 354.1$				(A) 30° (B) Ethyl bromide-ethyl iodide $P_A = 560.9$ $P_B = 161.8$			
	p_A/p_{AA}	p_B/p_{BB}	φ_A	φ_B	p_A/p_{AA}	p_B/p_{BB}	φ_A	φ_B
0.10	.984	1.680	— 1.79	2.54	0.9964	1.051	— 1.37	0.25
.2	.997	1.524	— 0.09	2.42	.9962	1.082	— 0.37	.50
.3	1.019	1.413	1.08	2.42	.9933	1.092	— .29	.75
.4	1.063	1.313	1.82	2.40	.9806	1.128	— .43	1.39
.5	1.119	1.220	1.99	2.34	.9627	1.162	— .61	2.52
.6	1.204	1.139	2.10	2.19	.9538	1.149	— .53	3.66
.7	1.345	1.082	2.28	2.17	.9508	1.130	— .42	5.82
.8	1.506	1.034	2.18	1.90	.9538	1.097	— .30	10.1
.9	1.758	1.008	2.17	1.66	.9449	1.058	— .28	24.1

The hexane-heptane mixtures are not included in Table III, because the linearity of the partial pressure curves shows that φ is 0. This supports the assumption involved in Langmuir's treatment that the energy, γ , be-

tween like surfaces, such as R-R, Br-Br, etc., is 0, since, for this system, Equation 3 simplifies to $\varphi = \gamma_{R-R}$ and $\varphi = 0$. The butyl chloride-butyl

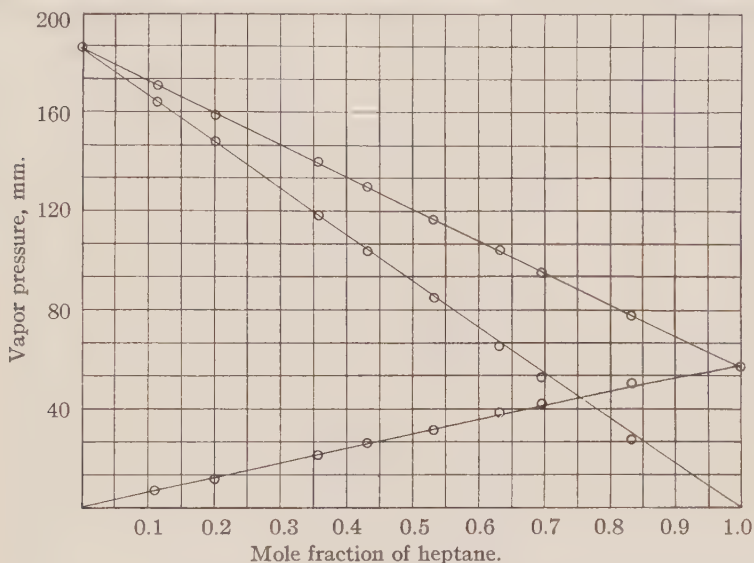


Fig. 2.—Hexane (A)-heptane (B) at 30°.

bromide mixtures are omitted from Table III because of the approximation of their curves to linearity and the heptane-ethyl iodide results at 30° are

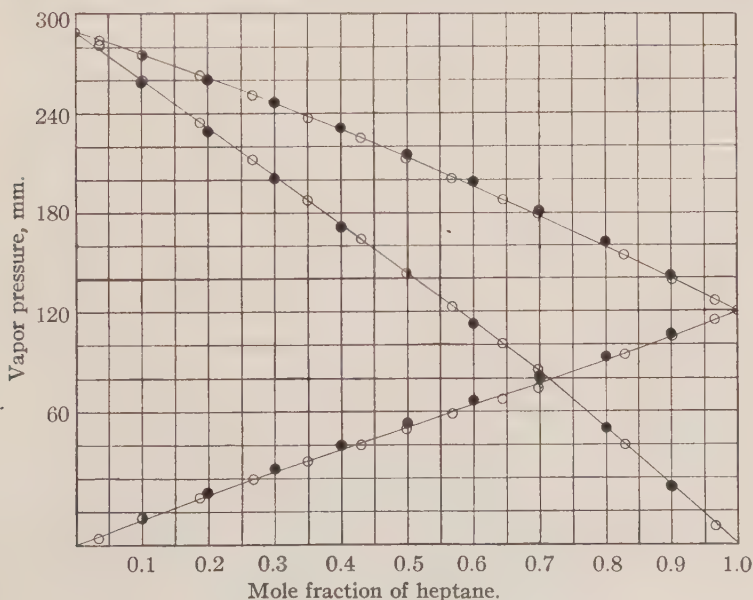


Fig. 3.—Carbon tetrachloride (A)-heptane (B) at 50°.

also omitted because of their resemblance to those at 50° , the values of φ at 30 and 50° differing by no more than the probable error. The results

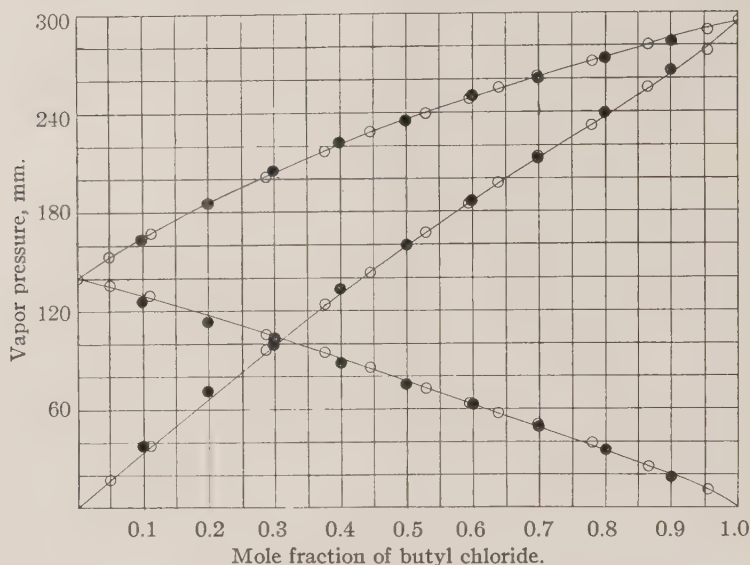


Fig. 4.—Heptane (A)—butyl chloride (B) at 50° .

are represented graphically in Figs. 2–9, in which the vapor pressures in mm. of mercury are plotted as ordinates against the mole fractions of

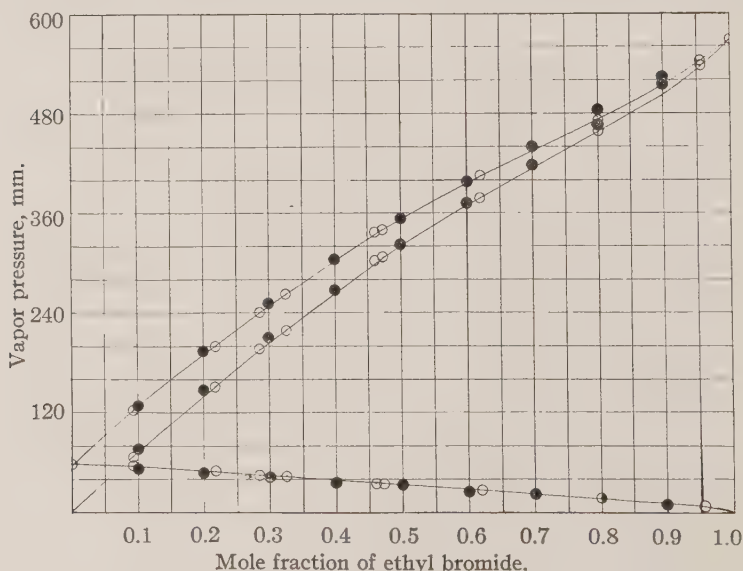


Fig. 5.—Heptane (A)—ethyl bromide (B) at 30° .

Component B as abscissas. The total pressure curve is, of course, uppermost and the partial pressure curve of Component B starts at the lower left-hand corner, while that of A starts at the lower right-hand corner. The experimental points are shown as hollow circles and the points calculated from φ as filled circles. Where the vapor pressure curves are straight, φ being 0, no calculated points are shown as they would obviously fall on the straight experimental lines. In the ethyl bromide-ethyl iodide system (Fig. 9) the departure from linearity is so slight as to render uncertain the value of φ , which is small in most of the mixtures and dependent upon concentration, as indicated by the curve in which the values of φ

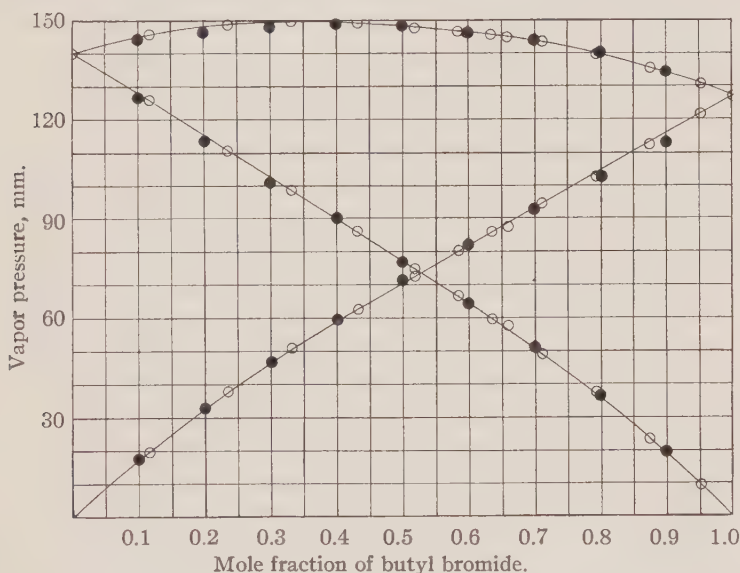


Fig. 6.—Heptane (A)—butyl bromide (B) at 50°.

obtained from the pressures of the ethyl iodide are plotted as ordinates, shown at the right of the diagram, against the mole fractions of ethyl iodide as abscissas. In spite of the smoothness of this curve, great importance cannot be attached to it because φ is calculated from such small deviations.

Since the values of φ calculated from individual vapor pressures are subject to a considerable variation, φ may advantageously be obtained by plotting the values of $\log p_A/p_{A4}$ in Equation 4 as ordinates against those of β^2 as abscissas, or of $\log p_B/p_{B4}$ against those of α^2 . If φ is constant, a straight line is thus obtained, the slope of which, when divided by $S_A/2.303kT$ or $S_B/2.303kT$, as the case may be, gives φ . The curves thus obtained for the heptane-ethyl iodide system show a tendency toward a slight deviation from linearity to give a curve with a point of inflection.

This deviation from linearity tends to increase with increasing difference in the polarity of the components. However, the curves are approximately linear for the systems heptane-butyl bromide, heptane-butyl chloride and heptane-carbon tetrachloride, and show no great deviation for heptane-ethyl bromide, although here the curvature is more pronounced. The

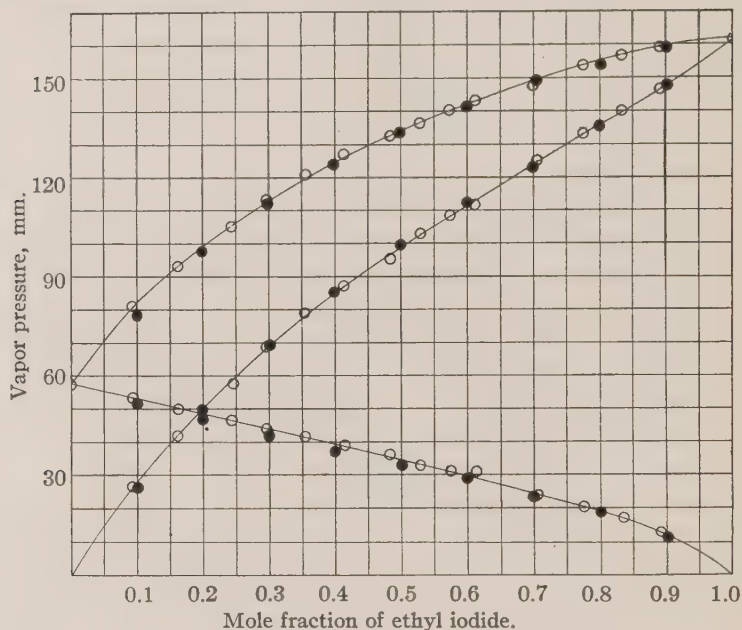


Fig. 7.—Heptane (A)—ethyl iodide (B) at 30°.

curves for the ethyl bromide-ethyl iodide system show no approach to linearity, so that no constant value of φ can be obtained to use in calculating γ . The value of φ for hexane-heptane is 0 and for butyl chloride-butyl bromide so small as to be indistinguishable from 0. These values of φ are used to calculate the values of γ shown in Table IV, in which the

TABLE IV
VALUES OF SURFACE ENERGY, γ

Substance	Surface area ($\text{\AA}^2$)	Interface	System	φ	γ (ergs./ cm^2)	γ (ergs./ cm^2) Langmuir
C_7H_{16}	154	R-Cl	$\text{C}_7\text{H}_{16}\text{-CCl}_4$	0.6	0.6	4.1
$\text{C}_4\text{H}_9\text{Cl}$	123	R-Cl	$\text{C}_7\text{H}_{16}\text{-C}_4\text{H}_9\text{Cl}$	1.14	10.0	
$\text{C}_2\text{H}_5\text{Br}$	99	R-Br	$\text{C}_7\text{H}_{16}\text{-C}_2\text{H}_5\text{Br}$	1.6	6.8	10.0
$\text{C}_4\text{H}_9\text{Br}$	125	R-Br	$\text{C}_7\text{H}_{16}\text{-C}_4\text{H}_9\text{Br}$	1.36	9.2	
$\text{C}_2\text{H}_5\text{I}$	104	R-I	$\text{C}_7\text{H}_{16}\text{-C}_2\text{H}_5\text{I}$ (30°)	2.52	7.9	13.7
Cl	41.5	R-I	$\text{C}_7\text{H}_{16}\text{-C}_2\text{H}_5\text{I}$ (50°)	2.29	7.2	
Br	48.1	Cl-Br	$\text{C}_4\text{H}_9\text{Cl-C}_4\text{H}_9\text{Br}$	0+	0+	
I	58.8	Cl-I		..	..	4.1

last column gives, for comparison, the values estimated by Langmuir. The molecules or radicals and their areas used in the calculation of the sixth column are shown in the first two columns. The calculation of the areas is, at best, a rough approximation, but, when the arbitrary character of the whole method of employing the molecular areas is considered, it becomes evident that the values assigned can have little significance as absolute quantities.

The value of γ_{R-Cl} determined from the heptane-carbon tetrachloride system should be the most accurate value in Table IV, for only two kinds

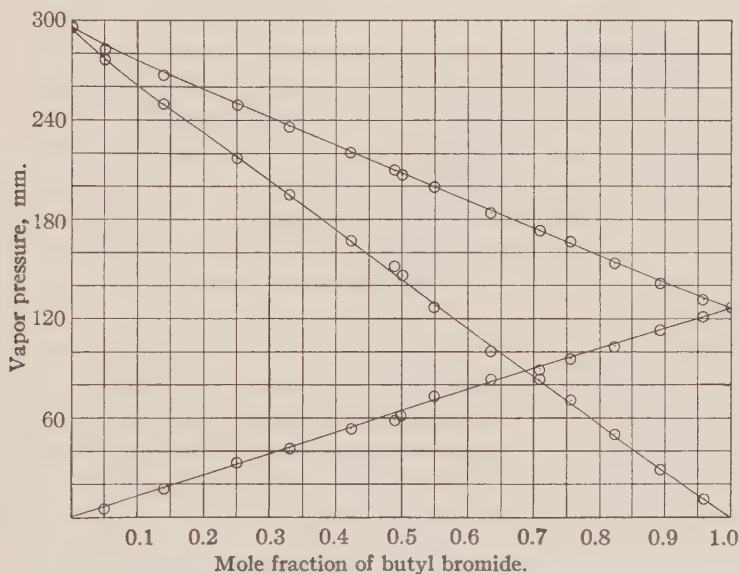


Fig. 8.—Butyl chloride (A)—butyl bromide (B) at 50°.

of surface being involved in the system, Equation 3 simplifies to $\phi = \gamma_{R-Cl}$, thus eliminating the doubtful fractions of surfaces. The value of γ_{R-Cl} determined from the heptane-butyl chloride system is very dependent upon the surface areas used, as shown by the fact that, when surface areas consistent with those of Langmuir are taken, a value of 37.0 is obtained instead of 10.0. It is certain that the great difference between the value of γ_{R-Cl} obtained from the carbon tetrachloride-heptane system and that from the heptane-butyl chloride system can be due only in part to experimental error or the use of incorrect surface areas, and must, therefore, be attributed to a more fundamental cause. The values of γ_{R-I} obtained from the heptane-ethyl iodide system, because of the different surface areas used, differ from Langmuir's figure which, in this one case, could be calculated directly from experimental data. When the values of the surface areas used by Langmuir are employed, good agreement is obtained at

30°. For the system butyl chloride–butyl bromide, φ is only approximately 0 and one can, therefore, say only that $\gamma_{\text{Cl-Br}}$ is small, presumably lower than Langmuir's value of 4.1 for $\gamma_{\text{Cl-I}}$, as the surface energy between chlorine and bromine might be expected to be less than that between chlorine and iodine.

These systems show linearity, in some cases very approximate, when $\log p_A/p_A^A$ is plotted against β^2 and $\log p_B/p_B^B$ against α^2 , and the experimentally determined vapor pressures may be satisfactorily reproduced by the use of a single value of φ , in spite of the considerable variation

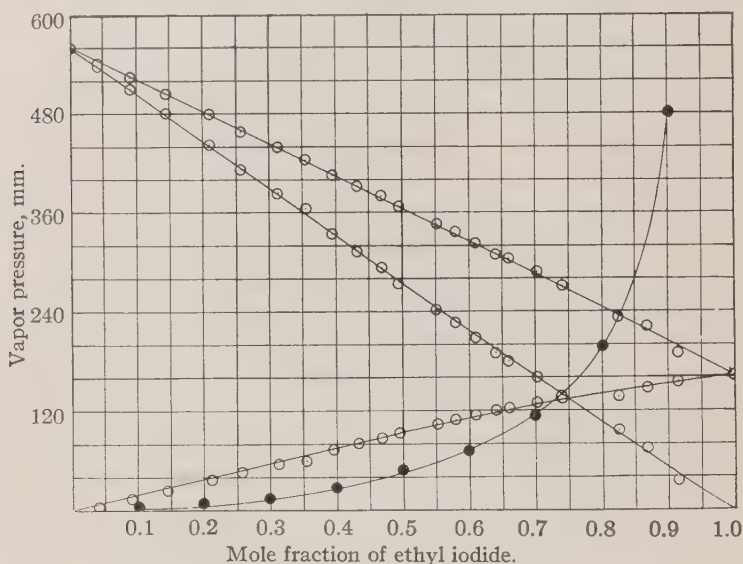


Fig. 9.—Ethyl bromide (A)–ethyl iodide (B) at 30°.

shown by the individual values of φ in Table III. The definitely established difference between the value of $\gamma_{\text{R-Cl}}$ obtained from the heptane–carbon tetrachloride system and that from the heptane–butyl chloride system is significant since it indicates that the energy between surfaces is not always dependent only upon the kinds of surface involved, thus showing that the principle of independent surface action is limited in its applicability. The carbon tetrachloride molecule has no electric moment, while the butyl chloride molecule contains a large dipole.⁵ The superposition of the forces of the dipole upon those of the chlorine surface presumably causes $\gamma_{\text{R-Cl}}$ as measured for the heptane–butyl chloride mixtures to be different from the energy between hydrocarbon and chlorine surfaces where no dipole is present. As these are dipoles of the same order of magnitude present in the other alkyl halides here studied, it is probable

⁵ Smyth, *Chem. Reviews* (1929).

that the values of γ obtained from these systems are all influenced more or less by the fields due to these dipoles, which may also affect the results by bringing about molecular orientation. It is apparent that the lack of generality of the principle of independent surface action and the frequent absence of random orientation, as well as the uncertainty in estimating surface areas, prevent the accurate determination of absolute values for the surface energies and limit the applicability of the theory. These results will be further discussed in a subsequent paper, where they will be contrasted with the behavior of systems containing an alcohol as one component.

II. SYSTEMS CONTAINING AN ALCOHOL

The apparatus described in Part I was used to determine the partial pressures of six different binary systems containing an alcohol as one of the components. The purification of the materials and the values of the physical constants used as criteria of their purity have been given in Part I.¹ Because of the somewhat different behavior of these systems containing an alcohol, it has been deemed advisable to treat them in a separate paper and contrast the results with those given by the supposedly normal liquids discussed in Part I. The experimentally determined partial pressures, p_A and p_B , of the components A and B are recorded in Table I, the composition of the mixtures being given in terms of the mole fraction B of the alcohol. The values of the partial pressures are interpolated graphically at intervals of 0.1 in the mole fraction of B and used to calculate the values of p_A/p_A^A , p_B/p_B^B , φ_A and φ_B , as was done in Part I,² the results being recorded in Table II. In Figs. 1-6 the vapor pressures in millimeters of mercury are plotted as ordinates against the mole fractions B as abscissas. The total pressure curve is uppermost and the partial pressure curve of the alcohol starts at the lower left-hand corner, while that of the other component, A, starts at the lower right-hand corner. The values of φ_A and φ_B are plotted as ordinates on the same diagrams against those of B as abscissas, the points being indicated by filled circles.

The partial pressure curve of ethyl alcohol in the heptane-ethyl alcohol system (Fig. 1) shows a small but well-defined rise to a maximum near $B = 0.94$. The phenomenon was at first attributed to a repeated error in the analysis, but careful checking of the method of analysis eliminated this possibility. The rise is found to decrease with rising temperature, which may be expected to reduce abnormalities arising from molecular association

¹ Smyth and Engel, *J. Am. Chem. Soc.*, **51**, 2646 (1929).

² See Langmuir, "Third Colloid Symposium Monograph," The Chemical Catalog Company, Inc., New York, 1925, p. 3.

or intermolecular action. No such maximum appears in the curves for the mixtures of ethyl alcohol with other substances than heptane, but in the heptane-butyl alcohol system (Fig. 2), the beginning of a rise is indicated from $B = 0.7$ to $B = 0.8$ which might lead to a maximum in the neighborhood of $B = 0.9$. Unfortunately, however, this region could not be investigated as the butyl alcohol mixtures containing a little heptane bumped so violently, apparently because of an abnormally high surface tension,

TABLE I

PARTIAL VAPOR PRESSURES OF BINARY MIXTURES (MM. OF HG)											
(A)	30°		(B)	(A)	50°		(B)	(A)	70°		(B)
Heptane-ethyl alcohol			Heptane-ethyl alcohol			Heptane-ethyl alcohol					
<i>B</i>	<i>p</i> _A	<i>p</i> _B	<i>B</i>	<i>p</i> _A	<i>p</i> _B	<i>B</i>	<i>p</i> _A	<i>p</i> _B			
0	58.2	0	0	141.1	0	0	301.4	0			
0.0400	56.0	22.0	0.0514	132.3	111.9	0.0567	265.9	234.4			
.0684	56.4	47.2	.1180	133.6	155.8	.1180	274.5	339.8			
.1236	56.4	56.1	.3022	130.5	176.9	.1573	272.8	375.2			
.2803	54.8	62.9	.4382	130.0	181.3	.2575	275.8	413.8			
.3342	54.5	63.5	.5862	126.6	184.7	.3633	274.3	431.6			
.5151	54.0	65.9	.6646	121.5	188.0	.4290	269.7	442.4			
.5934	51.8	68.1	.7327	120.0	191.3	.5069	269.0	446.7			
.7174	49.9	69.7	.7720	114.9	193.9	.5968	267.0	450.7			
.7687	47.9	71.0	.8230	106.2	198.6	.6648	259.6	458.1			
.8154	43.5	73.5	.8788	71.8	221.8	.7174	252.4	465.3			
.8550	40.6	73.9	.9274	47.2	234.5	.8689	251.0	462.8			
.8902	32.1	79.2	.9769	21.6	225.8	.8200	245.6	459.3			
.9173	18.4	87.9	1.0000	0	220.0	.8640	227.9	465.5			
.9545	10.1	87.0				.8940	183.1	493.4			
.9913	4.7	77.8				.9250	129.5	522.3			
1.0000	0	78.2				.9564	83.0	527.0			
						.9827	44.9	524.5			
						1.0000	0	539.1			
(A) 50°											
(A) 50°			(B)			(A) 30°					
Heptane-butyl alcohol			Butyl alcohol			Ethyl bromide-ethyl alcohol					
<i>B</i>	<i>p</i> _A	<i>p</i> _B	<i>B</i>	<i>p</i> _A	<i>p</i> _B	<i>B</i>	<i>p</i> _A	<i>p</i> _B			
0	140.5	0	0	308.9	0	0	567.8	0			
0.0688	135.6	13.8	0.0245	303.9	5.1	0.1175	527.1	40.7			
.1047	132.5	19.0	.1128	291.5	13.1	.2810	503.0	49.2			
.1980	130.0	21.2	.2236	280.4	15.7	.2997	502.2	47.1			
.2212	130.1	21.2	.3286	270.0	15.6	.4166	474.2	51.6			
.3641	126.6	22.0	.4164	256.7	18.2	.5431	447.9	53.5			
.5310	115.9	26.0	.5051	240.7	19.4	.6210	415.8	59.1			
.5429	114.9	25.8	.5241	236.0	18.6	.6784	389.6	60.9			
.6369	108.5	25.1	.6153	213.6	19.7	.7547	338.2	64.0			
.6400	109.0	26.9	.6839	189.5	20.5	.7562	339.8	63.8			
.6805	105.5	26.1	.7408	161.3	20.2	.8086	292.6	65.8			
.7388	94.2	29.3	.8234	125.3	21.1	.8553	240.2	68.4			
.7834	77.5	36.0	.8648	99.2	22.4	.8663	223.8	67.6			
1.0000	0	33.3	.9218	62.4	23.9	.8956	183.8	69.5			
			1.0000	0	33.3	1.0000	0	78.4			

TABLE I (Concluded)

(A) 50° (B)			(A) 30° (B)		
Butyl bromide-butyl alcohol			Ethyl iodide-ethyl alcohol		
B	p_A	p_B	B	p_A	p_B
0	127.0	0	0	162.3	0
0.1455	116.6	15.8	0.0438	162.4	25.9
.2140	113.6	17.3	.1307	152.9	44.9
.2594	111.2	18.4	.2886	148.2	53.1
.2815	109.6	19.0	.3668	145.3	55.3
.3898	104.9	20.9	.4000	144.4	56.2
.5033	97.6	22.4	.4875	139.8	57.1
.5226	97.1	21.9	.5507	137.3	59.6
.5790	92.5	22.7	.6259	132.1	61.8
.6368	86.2	23.3	.6854	125.8	63.3
.7093	78.7	24.3	.7384	116.7	64.9
.7751	67.5	25.3	.7836	106.5	66.2
.8832	43.3	27.2	.8195	97.4	68.4
.9383	26.3	27.9	.8483	88.2	69.4
.9739	16.2	27.5	.8912	72.1	70.0
1.0000	0	33.3	.9519	32.1	70.7
			1.0000	0	78.2

that the vapor pressures could not be measured. It appears that some complex formation may occur in this region of the heptane-alcohol mixtures, but the dielectric behavior of the mixtures shows no irregularity in

TABLE II

VALUES OF p_A/P_{AA} , p_B/P_{BB} AND φ								
(A) 30° (B)					(A) 50° (B)			
Heptane-ethyl alcohol					Heptane-ethyl alcohol			
$P_A = 58.2$			$P_B = 78.2$		$P_A = 141.1$			$P_B = 220.0$
B	p_A/P_{AA}	p_B/P_{BB}	φ_A	φ_B	p_A/P_{AA}	p_B/P_{BB}	φ_A	φ_B
0.1	1.069	6.778	55.8	10.7	1.053	6.727	47.4	11.2
.2	1.192	3.900	34.1	8.71	1.178	3.818	32.5	9.02
.3	1.350	2.685	22.8	7.45	1.336	2.667	23.0	7.76
.4	1.561	2.062	17.0	6.67	1.536	2.057	17.3	6.95
.5	1.856	1.688	13.4	6.17	1.814	1.673	13.7	6.39
.6	2.277	1.449	11.0	6.04	2.232	1.409	11.3	5.86
.7	2.921	1.270	9.52	6.04	2.882	1.227	9.58	5.51
.8	3.952	1.151	7.88	6.99	3.969	1.114	8.30	5.59

(A) 70° (B)					(A) 50° (B)			
Heptane-ethyl alcohol					Heptane-butyl alcohol			
$P_A = 301.4$			$P_B = 539.1$		$P_A = 140.5$			$P_B = 33.3$
0.1	1.018	5.832	(15.9)	10.8	1.060	5.560	29.6	8.13
.2	1.145	3.673	28.0	9.14	1.164	3.300	18.3	6.58
.3	1.308	2.542	22.3	7.71	1.303	2.201	13.4	5.37
.4	1.511	2.022	17.3	7.08	1.505	1.726	10.9	4.76
.5	1.778	1.655	13.8	6.50	1.715	1.441	8.19	4.33
.6	2.196	1.391	11.5	5.90	2.023	1.247	7.45	3.84
.7	2.856	1.203	9.90	5.14	2.410	1.157	6.37	4.23
.8	4.114	1.062	8.88	4.88				

TABLE II (Concluded)

(A) 50° (B)					(A) 30° (B)				
Carbon tetrachloride-butyl alcohol					Ethyl bromide-ethyl alcohol				
$P_A = 308.9$ $P_B = 33.3$					$P_A = 567.8$ $P_B = 78.4$				
B	p_A/P_{AA}	p_B/P_{BB}	φ_A	φ_B	p_A/P_{AA}	p_B/P_{BA}	φ_B	φ_B	
0.1	1.054	3.605	21.3	6.18	1.041	4.580	22.8	9.06	
.2	1.141	2.250	13.3	4.96	1.130	3.180	16.8	8.49	
.3	1.258	1.600	10.2	3.70	1.248	2.125	13.1	6.96	
.4	1.398	1.275	8.30	2.62	1.409	1.690	11.1	6.37	
.5	1.560	1.081	7.02	1.19	1.609	1.453	9.51	6.35	
.6	1.760	0.926	6.15	-1.82	1.875	1.275	8.44	6.22	
.7	1.953	.841	5.31	-7.22	2.230	1.146	7.63	6.00	
.8	2.170	.754	4.68	-26.4	2.642	1.052	6.85	4.85	
.9	2.522	.767	4.44	-98.5	3.170	0.993	6.19	-1.33	

(A) 50° (B)					(A) 30° (B)				
Butyl bromide-butyl alcohol					Ethyl iodide-ethyl alcohol				
$P_A = 127.0$ $P_B = 33.3$					$P_A = 162.3$ $P_B = 78.2$				
B	p_A/P_{AA}	p_B/P_{BB}	φ_A	φ_B	p_A/P_{AA}	p_B/P_{BA}	φ_B	φ_B	
0.1	1.042	3.694	17.8	6.22	1.068	5.115	41.1	9.65	
.2	1.126	2.628	12.4	5.70	1.163	3.601	22.6	8.36	
.3	1.238	1.952	9.77	5.05	1.301	2.293	16.8	7.45	
.4	1.382	1.577	8.16	4.58	1.473	1.790	13.4	6.82	
.5	1.555	1.321	6.98	3.95	1.716	1.491	11.4	6.48	
.6	1.779	1.152	6.20	3.05	2.067	1.300	10.3	6.37	
.7	2.073	1.030	5.64	1.10	2.543	1.169	9.24	6.43	
.8	2.480	0.946	5.26	-4.70	3.173	1.071	8.35	6.04	
.9	2.953	.918	4.85	-30.8	4.190	1.009	7.79	3.09	

this region and an attempt at explanation is unwise until more definite knowledge is obtained.

Table II shows that these systems deviate much more from Raoult's

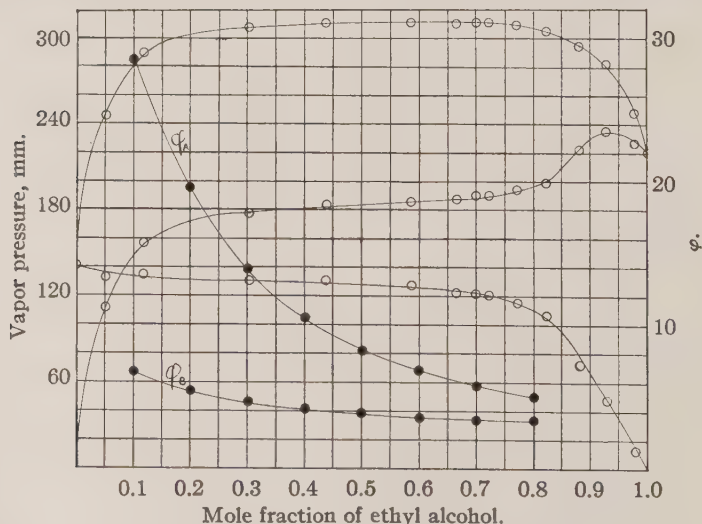


Fig. 1.—Heptane (A)—ethyl alcohol (B) at 50°.

law than do the normal liquids considered in Part I, the value of p_B/P_BB for $B = 0.1$ in the heptane (A)–ethyl alcohol (B) system at 30° being 6.778 as compared to the theoretical 1 of Raoult's law. The deviation of the partial pressure of a component from Raoult's law increases with decreasing concentration of the component. The values of φ are larger and vary more widely than those for the mixtures in Part I. Indeed, the variation of φ is so great that it is impossible to select a value from those in Table II for a system with any expectation of reproducing the partial pressures from it.

As an illustration of the manner in which a single value of φ fails to reproduce the experimentally observed vapor pressures, Fig. 4 shows as partly filled circles the pressures for the ethyl bromide–ethyl alcohol system, calculated by means of the Langmuir equation, the value of φ being

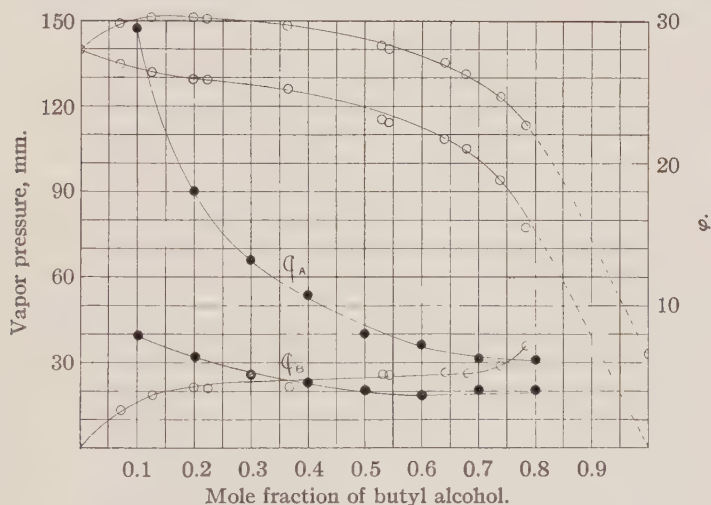


Fig. 2.—Heptane (A)—butyl alcohol (B) at 50° .

taken from Table III as 5.88. A similar failure in the calculation of the pressures has been found to occur in the other systems. The calculated points are, however, omitted from the other figures in order to avoid too great complication of the diagrams.

If $\log p_A/P_{AA}$ is plotted against β^2 and $\log p_B/P_{BB}$ against α^2 , straight lines are not obtained, as should be the case if φ were constant. When $\log (\log (p_A/P_{AA}))$ is plotted against $2 \log \beta$ and $\log (\log (p_B/P_{BB}))$ against $2 \log \alpha$, portions of the curves obtained are linear and average values of φ are calculated from these portions. The curves for the two components give somewhat different values of φ , but the values from the curves for the non-alcoholic components which are constant over a wider concentration range will be used in discussion.

For the sake of comparison, all the values are given in Table III together

with the values of the surface energy calculated from them, the values of γ from Part I being used when necessary in the calculation. The first column gives the interface for which γ is calculated, the second column the tem-

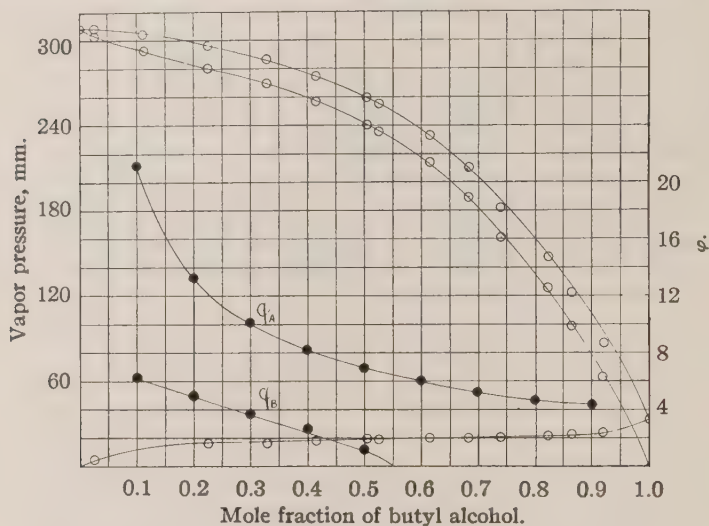


Fig. 3.—Carbon tetrachloride (A)—butyl alcohol (B) at 50°.

perature at which the vapor pressures were determined, the third under A gives the component from the partial pressures of which the values of ϕ in

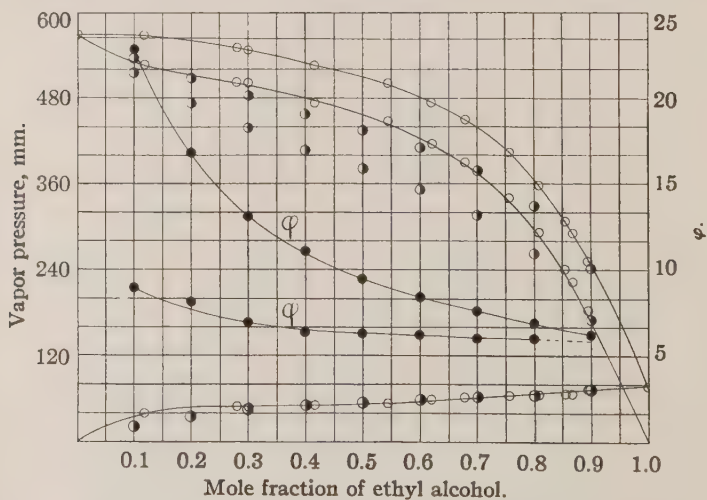


Fig. 4.—Ethyl bromide (A)—ethyl alcohol (B) at 30°.

the fourth column are obtained and the values of γ calculated from them are in the fifth column. The sixth column under B gives the alcohol from

the partial pressures of which the values of φ and γ in the remaining columns are calculated. At the foot of the table are given the values of γ used in calculating the surface energies for the halogen-hydroxyl interfaces, together with the surface areas (in square Ångströms) not previously used in Part I.

Possessed of the same uncertainties as the values obtained in Part I, these results are rendered more difficult of interpretation by the greater effect of molecular orientation in the mixtures. The energy at an interface where an hydroxyl group is involved is evidently so large in comparison with the energies at the other interfaces that the orientation of the alcohol molecules relative to one another must be more important in determining the behavior of the system than their orientation relative to the molecules of the other component or the orientation of the molecules of the other components relative to one another. For example, in an ethyl bromide-ethyl alcohol mixture at 30°, if an hydroxyl surface is in contact with bromine, γ is 64.9, if in contact with hydrocarbon, γ is 68.2, but, if in contact with another hydroxyl, γ is 0, while, if a bromine surface is in contact

TABLE III

VALUES OF φ AND γ FOR SYSTEMS CONTAINING AN ALCOHOL

Inter- face	$t, ^\circ\text{C.}$	A	φ	γ	B	φ	γ
R-OH	30	C_7H_{16}	5.77	68.2	$\text{C}_2\text{H}_5\text{OH}$	7.05	83.3
R-OH	50	C_7H_{16}	6.1	72.4	$\text{C}_2\text{H}_5\text{OH}$	7.6	89.9
R-OH	70	C_7H_{16}	6.78	80.2	$\text{C}_2\text{H}_5\text{OH}$	8.67	102.5
R-OH	50	C_7H_{16}	4.7	97.7	$\text{C}_4\text{H}_9\text{OH}$	6.4	133.1
Cl-OH	50	CCl_4	4.0	101.6 (80.8)	$\text{C}_4\text{H}_9\text{OH}$	7.25	95.7
Br-OH	30	$\text{C}_2\text{H}_5\text{Br}$	5.88	64.9	$\text{C}_2\text{H}_5\text{OH}$	8.34	81.8
Br-OH	50	$\text{C}_2\text{H}_5\text{Br}$	4.47	108.9 (92.4)	$\text{C}_4\text{H}_9\text{OH}$	6.65	134.6 (118.2)
I-OH	30	$\text{C}_2\text{H}_5\text{I}$	6.85	70.0	$\text{C}_2\text{H}_5\text{OH}$	6.67	68.9

Areas: OH = 24.7; $\text{C}_2\text{H}_5\text{OH}$ = 84.9; $\text{C}_4\text{H}_9\text{OH}$ = 112.5. Values of γ used in calculations: R-OH = 73.7 for $\text{C}_2\text{H}_5\text{OH}$; 97.7 for $\text{C}_4\text{H}_9\text{OH}$ (but values in parentheses are calculated from R-OH = 73.7); R-Cl = 0.6; R-Br = 6.8 for $\text{C}_2\text{H}_5\text{Br}$, 9.2 for $\text{C}_4\text{H}_9\text{Br}$; R-I = 7.9.

with hydrocarbon, γ is 6.8 as compared to 0 when the bromine is in contact with another bromine.

It is evident that when a butyl compound is used to obtain γ , the resulting value is higher than when an ethyl compound is used. Thus, the value of $\gamma_{\text{R-OH}}$ at 50° is 72.4 when ethyl alcohol is used and 97.7 when butyl is employed and $\gamma_{\text{Br-OH}}$ is 64.9 when the ethyl compounds are used and 108.9 in the butyl mixtures. Similarly, in Part I, it was found that the value obtained from the heptane-butyl bromide mixtures was higher than that from the heptane-ethyl bromide system. This difference could be largely eliminated by adjustment of the values of the surface areas, but, as these are derived by a consistent procedure from experimental data, their treatment as adjustable constants is not justifiable. The mean

value $\gamma_{R-OH} = 73.7$ is used in calculation where ethyl alcohol is concerned and the value 97.7 for the mixtures containing butyl alcohol, but, for the sake of comparison, the value 73.7 is also used with the latter and the results thus obtained are shown in parentheses. It is safer to compare molecules with the same hydrocarbon chain. One may thus conclude from the values for the ethyl compounds that γ_{R-OH} , γ_{Br-OH} and γ_{I-OH} are not very different from one another and, similarly, from those for the butyl compounds, that γ_{R-OH} , γ_{Cl-OH} and γ_{I-OH} differ little from one another, and that all are much larger than those for the interfaces considered which do not contain hydroxyl. The values in Table III are not sufficiently accurate to warrant their arrangement in a definite order, but

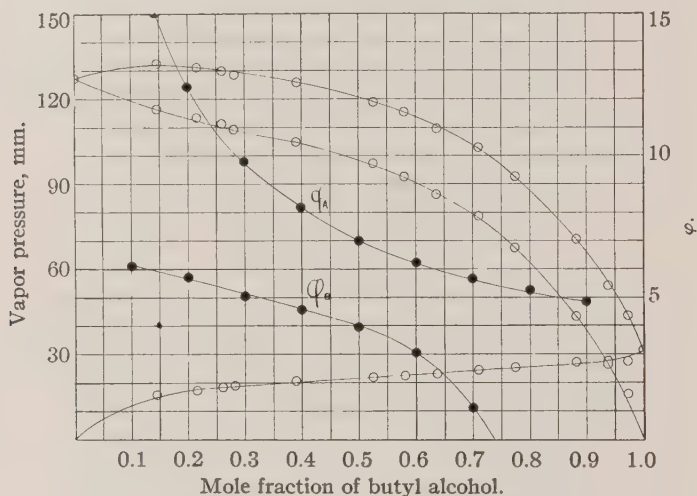


Fig. 5.—Butyl bromide (A)–butyl alcohol (B) at 50°.

it may be concluded that γ_{R-OH} , γ_{Cl-OH} and γ_{I-OH} are of the same order of magnitude and are much larger than the values for the hydrocarbon–halogen and halogen–halogen interfaces. The values of γ_{R-OH} and γ_{Br-OH} are quite different from those of Langmuir, 33.7 and 49.6, respectively, but when Langmuir's value 33.7 is used for γ_{R-OH} instead of 73.7 in calculating γ_{Br-OH} from the data for the ethyl bromide–ethyl alcohol system, the value 49.5 is obtained, which shows how dependent these results are upon one another as well as upon the uncertain surface fractions.

Langmuir examined the effect of molecular orientation in a hexane–ethyl alcohol mixture by means of a necessarily approximate method and was misled by a numerical error to the belief that the effect was very slight, but concluded that it might be important in some liquids, particularly in those whose molecules act as dipoles. Consequently, a second term was

introduced into the exponent of the original equation to take care of the energy of orientation in such liquids. When this equation is applied to these systems, a straight line is sometimes found but the frequent failure to obtain linearity shows that the equation is not generally applicable, although, of course, the mere presence of an additional adjustable constant renders it more capable of reproducing experimental data.

A general explanation of the deviations of the mixtures from normal behavior may be given in qualitative terms. The field of force around a molecule due to a doublet in its interior depends not merely upon the electric moment of the doublet, but also upon its location in the molecule. Thus the diethyl ether molecule has an electric moment of 1.14×10^{-18}

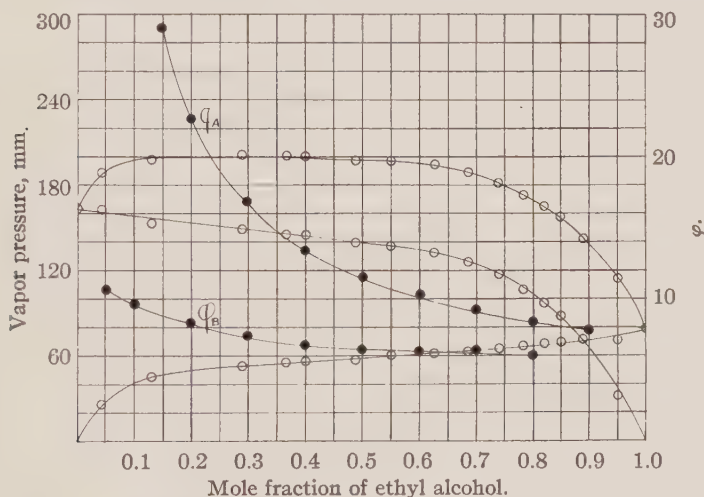


Fig. 6.—Ethyl iodide (A)–ethyl alcohol (B) at 30°.

e.s.u.,³ the resultant, presumably, of two dipoles located in the regions of attachment of the ethyl groups to the oxygen atom. The ethyl groups serve as a shield for the dipoles and thus prevent the molecule from being surrounded by a strong field of force. Ether, consequently, behaves as a normal unassociated liquid, even measurements of dielectric polarization at room temperature failing to give evidence of interference of the molecular force fields with one another. The ethyl alcohol molecule has two somewhat similar doublets located in the regions where the ethyl group and the hydrogen are attached to the oxygen atom, the resultant moment⁴ being 1.74×10^{-18} . The ethyl group may be pictured as partially screening one side of the molecule from the action of the doublets, but the doublets are close to the surface on the hydroxyl side of the molecule and a strong mo-

³ Stuart, *Z. Physik*, **51**, 1490 (1928).

⁴ Stranathan, *Phys. Rev.*, **31**, 653 (1928).

molecular field results. Alcohol, consequently, shows properties which cause it to be termed a highly associated liquid, and its dielectric behavior is abnormal in the extreme. The water molecule, of electric moment^{3,5} 1.8×10^{-18} , possesses two doublets similar to those in the alcohol molecule, but has no ethyl group to serve as a screen. The resultant powerful molecular field renders water a strongly associated and very abnormal liquid. If the higher alcohols are considered, it is evident that with increasing size of the hydrocarbon chain, which contains no appreciable doublets, the doublets at the hydroxyl group will be more and more screened from those in neighboring molecules and the effects of their fields thereby reduced. Consequently, the alcohols become less abnormal with increasing molecular weight.

Ethyl bromide, in spite of the moment, 1.86×10^{-18} , possessed by its molecule, is ordinarily termed a normal liquid.⁶ Its doublet should lie in the region of attachment of the ethyl group to the bromine atom and should thus be screened not only by the ethyl group but also by the large bromine atom, which should greatly reduce the molecular field as compared to that of the ethyl alcohol molecule. In ethyl iodide the screening effect of the large iodine atom should be greater than that of the bromine atom, and this, taken in conjunction with the slightly smaller moment of the molecule,⁷ 1.67×10^{-18} , should give a smaller molecular field. In conformity with this the dielectric behavior of the two substances shows that the ethyl bromide molecules affect one another more strongly than do those of ethyl iodide. This effect is also apparent in the vapor pressures given in Part I, for the heptane-ethyl bromide system shows a somewhat greater variation in the values of φ , presumably as the result of orienting forces, than is found in the heptane-ethyl iodide system. Butyl bromide, in which the longer hydrocarbon chain should reduce the effect of the molecular dipoles upon one another, shows but slight variation in the value of φ , and the heptane-butyl chloride mixtures behave similarly.

It appears that the deviations of liquids from the behavior required by the Langmuir equation may be qualitatively explained in terms of the forces acting between the molecular dipoles. Forces which greatly restrict the freedom of orientation of the dipoles in an externally applied electric field may yet be insufficient to impair seriously the validity of the Langmuir equation. As the effects of the dipoles upon one another depend not only upon their electric moments but also upon their location in the molecules and upon the sizes and shapes of these molecules and probably upon the electronic constraints in them, it appears impossible to formulate any generally valid expression for the exact quantitative representation of the

³ Williams, *Physik. Z.*, **29**, 204 (1928).

⁶ Smyth and Morgan, *J. Am. Chem. Soc.*, **50**, 1547 (1928).

⁷ Value recently obtained in this Laboratory by Mr. W. N. Stoops.

interaction of molecular dipoles. Evidently the assumptions upon which the Langmuir equation is derived are too simple to permit of its general and exact application, but the approximate agreement between the calculated and the observed results for the less polar liquids and the general trend of the surface energies calculated indicate that the theory bears a relation to fact beyond a mere resemblance of the equation to the Duhem thermodynamic equation, and the idea of molecular surface energies may lead to most interesting results in spite of the difficulties in its exact quantitative application.

ACKNOWLEDGMENT

The author wishes to acknowledge his indebtedness to Prof. Charles P. Smyth who not only suggested the problem but rendered invaluable assistance in the form of helpful criticism and advice.

